

PATENT SPECIFICATION

(11) 1 522 441

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- (21) Application No. 6527/76 (22) Filed 19 Feb. 1976 *
 (23) Complete Specification filed 28 Jan. 1977
 (44) Complete Specification published 23 Aug. 1978
 (51) INT CL² C08F 2/44
 (52) Index at acceptance
 C3P KP
 C3R 1A IC CI C5BI C6AX C6X C8P C8R L3A L3C L4F
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(54) PHENOL-ALDEHYDE RESIN-IMPREGNATED PREPREGS

(71) We, CIBA-GEIGY AG, a Swiss Body Corporate of Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to a method for the production of reinforced composites from photopolymerisable and thermosettable compositions and reinforcing materials, and to the composites so obtained by this method.

Composite structures are commonly made by impregnating fibrous materials, such as paper, glass, and carbon fibres, with a solution of a solid thermosettable resin and a heat-activated curing agent for the resin, causing the resin to solidify by evaporation of the solvent, and, when desired, curing the resin composition by the action of heat. Composite structures may also be prepared from films of a thermosettable resin composition by laying a film of the resin composition on a fibrous reinforcement and applying heat and pressure so that the resin composition flows about the fibres but remains curable, and then heating further when desired so that the resin composition is cured by the heat-activated curing agent. Both these methods suffer from certain drawbacks.

If a solvent is used, it is not always possible to eliminate all traces of it before the final curing takes place. In consequence, the final composite may contain voids caused by evaporation of such residual solvent. Further, use of solvents may cause difficulties due to their toxicity or inflammability, or to pollution. When a film adhesive is used, it must first be cast from a liquid thermosettable resin and this is then advanced to the solid state. Such a process adds considerably to the cost of the composite. Both methods also require a considerable expenditure of energy, either to evaporate solvents or to advance the resin.

We have now found a method by which reinforcing materials may be impregnated with a liquid, solvent-free resin composition

and this composition rapidly converted into a solid, but still heat-curable, state without the inconvenience of the prior art methods. In this novel method, a liquid resin composition, comprising a thermally-curable phenolic resin and a photopolymerisable component, after being used to impregnate the reinforcing material, is photopolymerised by exposure to actinic radiation, optionally in the presence of a photosensitising agent, but not thermally crosslinked, and the resultant prepreg is, when desired, fully cured by heating to form the composite.

Accordingly, the present invention provides a method for the preparation of prepregs which comprises

i) impregnating a fibrous reinforcing material with a liquid composition containing both a thermosettable phenol - aldehyde resin and at least one photopolymerisable component (other than a phenol - aldehyde resin) and, if required, a heat-curing agent for the phenol - aldehyde resin, and

ii) exposing the impregnated material to actinic radiation such that the said composition solidifies due to photopolymerisation of the said photopolymerisable component while the phenol - aldehyde resin remains substantially in the thermosettable state.

There are also provided prepregs prepared by the method of this invention.

There are further provided a method of preparing a reinforced composite which comprises heat-curing a photopolymerised, but still thermosettable, prepreg of this invention, and reinforced composites prepared by this method.

Compositions used to prepare the prepregs of the present invention must be liquid under the conditions used in making the prepregs but are preferably solvent-free.

The photopolymerisable component used in the compositions employed in the present invention may be of any chemical type known to polymerise under the influence of actinic radiation. Such materials are described in, for example, Kosar, "Light-sensitive Systems: Chemistry and Applications of Non-Silver

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Halide Photographic Processes", Wiley, New York, 1965, 473 pp.

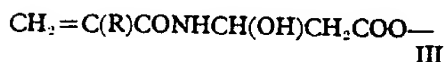
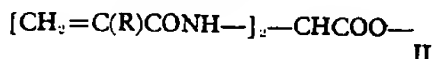
As is well known, such components fall into two main classes

(a) those which are polymerised through a free-radical chain reaction (photoinitiated polymerisation) and

(b) those in which polymerisation is effected by reaction of an excited monomer molecule with another monomer molecule.

The first type require only one photopolymerisable group per molecule to form long chains on polymerisation, while the second type must have at least two photopolymerisable groups per molecule, since if they have only one such group per molecule they will dimerise but not polymerise on irradiation.

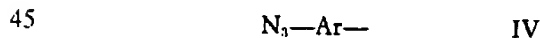
Photopolymerisable substances of the first type preferred for use in this invention have one ethylenic linkage, or more than one providing they are unconjugated. Examples of these substances are acrylic esters containing at least one group of the general formulae I, II, or III



where R is a hydrogen, chlorine, or bromine atom, or an alkyl hydrocarbon group of 1 to 4 carbon atoms, especially a methyl group. Other examples are styrene and crotonic acid.

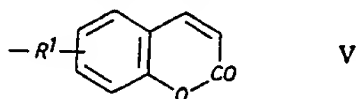
Photopolymerisable materials of the second type include those having at least two, and preferably three or more, groups which are azido, coumarin, stilbene, maleimide, pyridinone, chalcone, propenone, or pentadienone, or acrylic acid groups which are substituted in their 3-position by groups having ethylenic unsaturation or aromaticity in conjugation with the ethylenic double bond of the acrylic group.

Examples of suitable azides are those containing at least two groups of the formula



where Ar denotes a mononuclear or dinuclear aromatic radical containing from 6 to 14 carbon atoms, especially a phenylene or naphthylene group.

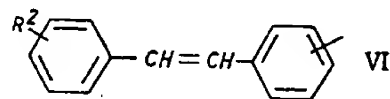
Examples of suitable coumarins are those containing at least two groups of the formula



where R¹ is an oxygen atom, a carbonyloxy

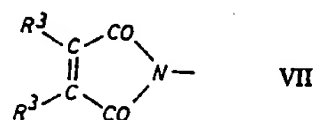
group (—COO—), a sulphonyl group, or a sulphonyloxy group.

Examples of those containing stilbene groups are those containing at least two groups of the formula



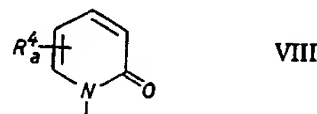
where R² is the residue, containing up to 8 carbon atoms in all, of a five or six-membered nitrogen-containing heterocyclic ring fused to a benzene or naphthalene nucleus and linked through a carbon atom of the said heterocyclic ring adjacent to a nitrogen hetero atom thereof to the indicated benzene nucleus, such as a benzimidazolyl or a naphthotriazolyl group.

Examples of those containing maleimide units are those having at least two groups of the formula



where each R³ is an alkyl group of 1 to 4 carbon atoms, a chlorine or bromine atom, or a phenyl group, especially a methyl group.

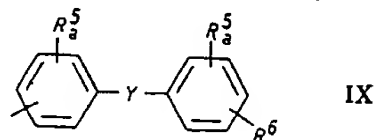
Examples of those containing pyridinone units are those containing at least two groups of the formula



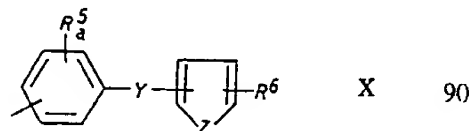
where

R⁴ is an aliphatic or cycloaliphatic radical of 1 to 8 carbon atoms, and
a is zero or an integer of 1 to 4.

Examples of compounds containing chalcone, propenone, and pentadienone groups are those containing at least two groups of the formula



or



where

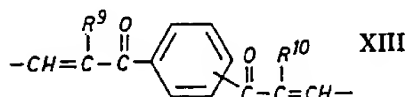
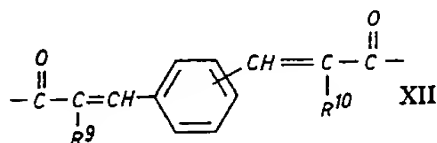
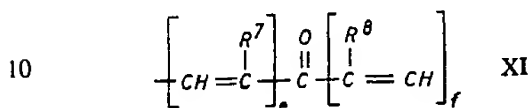
each R⁵ is a halogen atom, or an alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkoxy, cycloalkoxy, alkenoxy, cycloalkenoxy, carbalkoxy, carbocycloalkoxy, carbalkenoxy, or

carbocycloalkenoxy group, such organic groups containing 1 to 9 carbon atoms, or is a nitro group, or a carboxyl, sulphonic, or phosphoric acid group in the form of a salt,

5 α has the meaning previously assigned,

R^6 represents a valency bond or a hydrogen atom,

Y represents a chain of carbon atoms containing in that chain a grouping of formula



15 R^7 and R^8 are each individually a hydrogen atom, an alkyl group preferably of 1 to 4 carbon atoms, or an aryl group, preferably a mononuclear group such as a phenyl group, or R^7 and R^8 conjointly denote a polymethylene chain of 2 to 4 methylene groups;

20 R^9 and R^{10} are each a hydrogen atom, an alkyl group preferably of 1 to 4 carbon atoms, or an aryl group, preferably a mononuclear group such as a phenyl group,

25 e and f are each zero, 1, or 2, with the proviso that they are not both zero, and

Z is an oxygen or sulphur atom.

Suitable 3-substituted acrylates are those containing at least two groups of the general formula



30 where

R^{11} is an aliphatic or mononuclear aromatic, araliphatic, or heterocyclic group, preferably of up to 12 carbon atoms, having ethylenic unsaturation or aromaticity in conjugation with the double bond shown such as a prop-2-enyl, phenyl, 2-furyl, 2- or 3-pyridyl, or styryl group, and

R has the meaning previously assigned.

40 Specific examples are disorbates of poly(oxyethylene) glycols and poly(oxypropylene) glycols.

If desired, a mixture of photopolymerisable compounds may be used.

45 Especially preferred photopolymerisable components used in the method of this invention are esters of acrylic and methacrylic acid, such as 1-acryloxy-2-hydroxy-3-phenoxypropane and especially diacrylates and dimethacrylates of dihydric and trihydric

50 alcohols, especially of aliphatic alcohols containing from 2 to 10 carbon atoms, such as 1,2-bis(acryloxy)ethane, 1,3-bis(acryloxy)propane, 1,4-bis(acryloxy)butane, 1,3-bis(acryloxy)-2,2-dimethylpropane, 1,2-bis(3-hydroxypropoxy)-2-hydroxypropoxy)ethane, 1,3-bis(3-acryloxy-2-hydroxypropoxy)propane, 1,4-bis(3-acryloxy-2-hydroxypropoxy)butane, 1,3-bis(3-acryloxy-2-hydroxypropoxy)-2,2-dimethylpropane, and the corresponding methacrylates.

60 Phenolic resins used in accordance with the present invention may be any resol or novolak prepared from a phenol and an aldehyde under acid or alkaline conditions. Suitable phenols include phenol itself, 65 resorcinol, alkyl-substituted phenols, such as cresols, xylenols, and tertiary butyl phenols, and aryl-substituted phenols, especially *p*-phenylphenol. The aldehyde which is condensed with the phenol is preferably formaldehyde but other aldehydes such as acetaldehyde and furfuraldehyde may also be used. Preferred phenolic resins are novolaks, especially those made from phenol itself and formaldehyde. 75

The molar ratio of photopolymerisable component to phenol-aldehyde resin in the compositions is generally from 1:10 to 10:1, ratios from 1:5 to 5:1 being preferred.

80 Preferably the photopolymerisable component is irradiated in the presence of a photopolymerisation catalyst therefor.

Photopolymerisation catalysts suitable for use in the present invention are well known and are described in, for example, the book by Kosar cited above. The catalysts fall into two main classes,

(a) those which, on irradiation, give an excited state that leads to the formation of free radicals which then initiate polymerisation of the monomer (photoinitiators) and

(b) those which, on irradiation, give an excited state which in turn transfers its energy to a monomer molecule giving rise to an excited molecule which then crosslinks with another monomer molecule (photosensitisers).

95 The first class includes organic peroxides and hydroperoxides, α -halogen substituted acetophenones such as 2,2,2-trichloro-4'-*tert*-butylacetophenone, benzoin and its alkyl ethers, e.g., the *n*-butyl ether, benzophenones, *O*-alkoxycarbonyl derivatives of an oxime of benzil or 1-phenylpropane-1,2-dione, such as benzil (*O*-ethoxycarbonyl)- α -monoxime and 1-phenylpropane-1,2-dione-2-(*O*-ethoxycarbonyl)oxime, benzil acetals, e.g., its dimethyl acetal, and mixtures of phenothiazine dyes (e.g., methylene blue) or quinoxalines (e.g., metal salts of 2-(*m*- or *p*-methoxyphenyl)quinoxaline-6'- or 7'-sulphonic acids) with electron donors such as sodium benzenesulphonate or other sulphonic acid or a salt thereof, an arsine, a phosphine, or

thiourea (photoredox systems), these initiators being used with unsaturated esters, especially acrylates and methacrylates, and also acrylamides.

5 The photosensitisers include 5 - nitroacenaphthene, 4 - nitroaniline, 2,4,7 - trinitro - 9 - fluorenone, 3 - methyl - 1,3 - diaza - 1,9 - benzanthrone, and bis(dialkylamino)benzophenones, especially Michler's ketone, i.e., bis(*p* - dimethylamino)benzophenone.

10 Generally, 0.1 to 20%, and preferably 0.5 to 15% by weight, of the photopolymerisation catalyst is incorporated, based on the weight of the photopolymerisable component.

15 The reinforcement may be in the form of woven or nonwoven sheets, unidirectional lengths, or chopped strands and may be of natural or synthetic fibres, especially glass, boron, stainless steel, tungsten, silicon carbide, asbestos, an aromatic polyamide, or carbon.

20 In the photopolymerising step actinic radiation of wavelength 200-600 nm is preferably used. Suitable sources of actinic radiation include carbon arcs, mercury vapour arcs, fluorescent lamps with phosphors emitting ultraviolet light, argon and xenon glow lamps, tungsten lamps, and photographic flood lamps. Of these, mercury vapour arcs, particularly sun lamps, fluorescent sun lamps, and metal halide lamps are most suitable. The time required for the exposure of the photopolymerisable component will depend upon a variety of factors which include, for example, the individual substance used, the amount of that substance on the reinforcement, the type of light source, and its distance from the impregnated material. Suitable times may be readily determined by those familiar with photopolymerisation techniques, but the product so photopolymerised must still be curable by heating. Of course, irradiation is carried out at a temperature below that at which substantial heat-curing would occur.

45 Phenol - aldehyde novolaks are used, with as heat-curing agent, a substance liberating formaldehyde under the action of heat, such as paraform but usually hexamethylenetetramine. Resols may, if desired, be applied with a latent acid catalyst. The heat-curing agent is usually dissolved or suspended in the liquid composition before impregnation of the reinforcement. The temperatures, and the amount of formaldehyde - liberator or latent acid catalyst, required for thermal curing are readily found by routine experimentation and easily derivable by those skilled in the art from what is already well known concerning the heat-curing of phenolic resins.

60 The photopolymerisable, thermally curable compositions, including any heat-curing agent for the phenol - aldehyde resin and any photopolymerisation catalyst for the photopolymerisable component, are preferably applied to the reinforcing material so that the prepreg

contains 20 to 80% by weight of the said composition and, correspondingly, 80 to 20% by weight of the reinforcement. More preferably, 30 to 50% by weight of the composition and 70 to 50% by weight of the reinforcement are employed.

70 Products made in accordance with the present invention may be in the form of flat sheets or shaped articles. When a hollow shaped article is required, it is particularly convenient to impregnate a continuous tow of fibrous reinforcing material, and wind the tow around a former while at the same time exposing it to actinic radiation. Such windings still have a certain degree of flexibility, permitting the former to be removed more easily than when a rigid winding is formed in one step. When desired, the winding may be heated to complete the cure.

80 The following Examples illustrate the invention. Temperatures are in degrees Celsius, and, unless otherwise indicated, parts are by weight. The epoxide content was determined by titration against a 0.1N solution of perchloric acid in glacial acetic acid in the presence of excess of tetraethylammonium bromide, crystal violet being used as the indicator.

85 All interlaminar shear strengths quoted are the mean of three results and were determined by ASTM method D 2344-72. "Resin-forming content" denotes the percentage residue left after a 1 g sample of the material has been heated in a 5 cm diameter dish in an oven at 120° for 3 hours at atmospheric pressure.

EXAMPLE 1

90 Benzoin *n* - butyl ether (2 parts) and hexamethylenetetramine (4 parts) were added to a mixture of the bisacrylate of 2,2 - dimethyl - 1,3 - propanediol (50 parts) with a solid phenol - formaldehyde novolak resin of number average molecular weight 420 which had a phenol - formaldehyde molar ratio of 1:0.72 (50 parts). This liquid composition was used to impregnate glass cloth (square weave). The impregnated glass cloth was exposed on both sides to a 500 W medium pressure mercury vapour lamp at a distance of 15 cm for 60 seconds. The composition became solid as photopolymerisation proceeded.

110 A 6-ply glass cloth laminate was then made by pressing six 15 cm square pieces of the prepreg at 170° for 1 hour at a pressure of 2.1 MN/m². This laminate, which consisted of 25.4% of resin and 74.6% of glass, had an interlaminar shear strength of 15.5 MN/m². After the laminate had been immersed in boiling water for 2 hours its interlaminar shear strength was still 8.6 MN/m².

EXAMPLE 2

First, 1,4 - bis(3 - methacryloxy - 2 -

hydroxypropoxy)butane, the photopolymerisable component, was prepared *in situ*. Methacrylic acid (3137.3 g), triethylamine (21.1 g), and hydroquinone (7.8 g) were stirred at 120° and 4000 g of butane - 1,4 - diol diglycidyl ether (having an epoxide content of 9.12 equiv./kg) containing 6.4 g of hydroquinone was added over 2½ hours. The mixture was then stirred at 120° for a further ½ hour, by which time its epoxide content was negligible.

Hexamethylenetetramine (4 parts) and benzoin *n* - butyl ether (2 parts) were added to a 3:1 mixture (100 parts) of the above dimethacrylate and the phenol - formaldehyde novolak resin used in Example 1. The liquid composition was used to make a prepreg as described in Example 1, except that the impregnated glass cloth was irradiated for only 5 seconds. A six-ply laminate was prepared as described in Example 1. This laminate, which consisted of 32.9% of resin and 67.2% of glass, had an interlaminar shear strength of 19.5 MN/m².

EXAMPLE 3

A woven cloth consisting of poly(*p* - phenylene terephthalamide) fibres was coated with a composition comprising 70 parts of a phenol - formaldehyde resol, 30 parts of 1 - acryloxy - 2 - hydroxy - 3 - phenoxypropane (prepared as described in British Patent Specification No. 1407813), and 1 part of benzil dimethyl acetal. The resol had a resin-forming content of 78% and the molar ratio of phenol:formaldehyde was 1:1.6.

A prepreg so prepared was irradiated for 30 seconds with a high pressure metal halide quartz lamp. A good laminate was prepared by pressing six 15×15 cm pieces of this prepreg at 150° under a pressure of 2.1 MN/m², the pressure being released after 2 and 4 minutes to allow the escape of volatile materials.

EXAMPLE 4

A good six ply laminate was made as described in Example 3, using unidirectional carbon fibres in place of the polyamide fibres and irradiating for one minute.

EXAMPLE 5

A polyoxyethylene disorbate was prepared as follows.

To a stirred mixture of 100 g of a poly-(oxyethylene) glycol, average molecular weight 200, 110 g of triethylamine, and 50 ml of toluene at room temperature was added 130.5 g of sorbyl chloride over 30 minutes. The mixture was stirred at 80° for 1 hour, cooled to room temperature, and then filtered, and the solvent was distilled off under reduced pressure to leave the desired disorbate.

A carbon fibre prepreg was made, the fibres being coated with a composition com-

prising 30 parts of the disorbate, 70 parts of the phenol - formaldehyde novolak used in Example 1, 4 parts of hexamethylenetetramine, and 1 part of Michler's ketone. The prepreg was irradiated on each side for 15 minutes with a 400 w high pressure metal halide quartz arc lamp, and a six ply laminate was made by pressing at 170° for 1 hour under a pressure of 2.1 MN/m².

EXAMPLE 6

A six ply laminate was made in the same way as described in Example 5, using poly(*p* - phenylene terephthalamide) fibres. In place of such fibres there could be employed in a like manner poly(*m* - phenylene isophthalamide) fibres.

WHAT WE CLAIM IS:—

1. A method for the preparation of prepreps which comprises

i) impregnating a fibrous reinforcing material with a liquid composition containing both a thermosettable phenol - aldehyde resin and at least one photopolymerisable component (other than a phenol - aldehyde resin) and

ii) exposing the impregnated material to actinic radiation such that the said composition solidifies due to photopolymerisation of the said photopolymerisable component while the phenol - aldehyde resin remains substantially in the thermosettable state.

2. A method according to claim 1, in which the molar ratio of photopolymerisable component to phenol - aldehyde resin in the composition is from 1:10 to 10:1.

3. A method according to claim 2, in which the said molar ratio is from 1:5 to 5:1.

4. A method according to any preceding claim, in which actinic radiation of wavelength 200—600 nm is used.

5. A method according to any preceding claim, in which the prepreg is made by impregnating a continuous tow of fibrous reinforcing material and winding the tow around a former while at the same time exposing it to actinic radiation.

6. A method according to any preceding claim, in which the fibrous reinforcing material comprises glass, boron, stainless steel, tungsten, silicon carbide, asbestos, an aromatic polyamide, or carbon.

7. A method according to any preceding claim, in which the phenol - aldehyde resin is a resol or novolak from phenol, resorcinol, or an alkyl- or aryl - substituted phenol.

8. A method according to claim 7, in which the alkyl - substituted phenol is a cresol, a xlenol, or a tertiary butyl phenol and the aryl - substituted phenol is *p* - phenylphenol.

9. A method according to any preceding

claim, in which the phenol - aldehyde resin - is made from formaldehyde.

10. A method according to any preceding claim, in which the phenol - aldehyde resin is a novolak employed in the presence of, as heat-curing agent therefor, a substance liberating formaldehyde under the action of heat.

11. A method according to claim 10, in which the formaldehyde - liberating substance is hexamethylenetetramine.

12. A method according to any preceding claim, in which the photopolymerisable component is irradiated in the presence of a photopolymerisation catalyst therefor.

13. A method according to claim 12, in which the photopolymerisation catalyst comprises 0.1 to 20% by weight, based on the weight of the photopolymerisable component.

14. A method according to claim 13, in which the photopolymerisation catalyst comprises 0.5 to 15% by weight, based on the weight of the photopolymerisable component.

15. A method according to any preceding claim, in which the phenol - aldehyde resin and the photopolymerisable substance, together with any heat-curing agent for the phenol - aldehyde resin and any photopolymerisation catalyst for the photopolymerisable component, constitute from 20 to 80% by weight of the prepreg.

16. A method according to claim 15, in which the phenol - aldehyde resin and the photopolymerisable substance, together with any heat-curing agent for the phenol - aldehyde resin and any photopolymerisation catalyst for the photopolymerisable component, constitute from 30 to 50% by weight of the prepreg.

17. A method according to any preceding claim, in which the photopolymerisable component is photopolymerised through a free-radical chain reaction.

18. A method according to any of claims 1 to 16, in which the photopolymerisable component is photopolymerised by reaction of an excited monomer molecule with another monomer molecule.

19. A method according to claim 17, in which the photopolymerisable component has one ethylenic linkage or, providing they are unconjugated, more than one.

20. A method according to claim 19, in which the photopolymerisable component is an acrylic ester containing at least one group of formula



or



where R is a hydrogen, chlorine, or bromine

atom, or an alkyl hydrocarbon group of 1 to 4 carbon atoms.

21. A method according to claim 20, in which the acrylic ester is a diacrylate or dimethacrylate of a dihydric or trihydric alcohol.

22. A method according to claim 21, in which the alcohol is an aliphatic compound of 2 to 10 carbon atoms.

23. A method according to claim 18, in which the photopolymerisable component contains at least two groups which are azido, coumarin, stilbene, maleimide, pyridinone, chalcone, propenone, or pentadienone, or acrylic acid groups which are substituted in their 3-position by groups having ethylenic unsaturation or aromaticity in conjugation with the ethylenic double bond of the acrylic group.

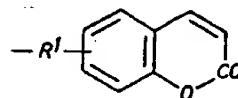
24. A method according to claim 23, in which the photopolymerisable component contains at least two groups of the formula



where Ar denotes a mononuclear or dinuclear aromatic radical containing from 6 to 14 carbon atoms.

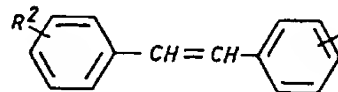
25. A method according to claim 24, in which Ar denotes a phenylene or naphthylene group.

26. A method according to claim 18, in which the photopolymerisable component contains at least two groups of the formula



where R¹ is an oxygen atom, a carbonyloxy group ($-\text{COO}-$), a sulphonyl group, or a sulphonyloxy group.

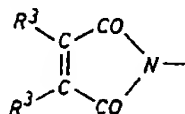
27. A method according to claim 18, in which the photopolymerisable component contains at least two groups of the formula



where R² is the residue, containing up to 8 carbon atoms in all, of a five or six-membered nitrogen-containing heterocyclic ring, fused to a benzene or naphthalene nucleus and linked through a carbon atom of the said heterocyclic ring adjacent to a nitrogen hetero atom thereof to the indicated benzene nucleus.

28. A method according to claim 27, in which R² denotes a benzimidazolyl or naphthotriazolyl group.

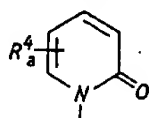
29. A method according to claim 18, in which the photopolymerisable component contains at least two groups of the formula



where each R^3 is an alkyl group of 1 to 4 carbon atoms, a chlorine or bromine atom, or a phenyl group.

30. A method according to claim 29, in which each R^3 denotes a methyl group.

31. A method according to claim 18, in which the photopolymerisable component contains at least two groups of the formula

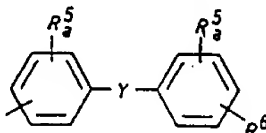


where

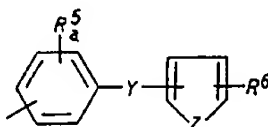
R^4 is an aliphatic or cycloaliphatic radical of 1 to 8 carbon atoms, and

a is zero or an integer of 1 to 4.

32. A method according to claim 18, in which the photopolymerisable component contains at least two groups of the formula



or



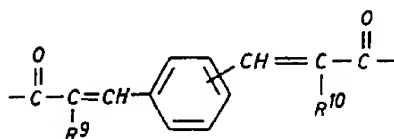
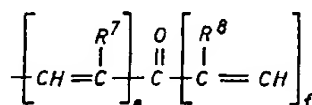
where

each R^5 is a halogen atom, or an alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkoxy, cycloalkoxy, alkenoxy, cycloalkenoxy, carbalkoxy, carbocycloalkoxy, carbalkenoxy, or carbocycloalkenoxy group, such organic groups containing 1 to 9 carbon atoms, or is a nitro group, or a carboxyl, sulphonc, or phosphoric acid group in the form of a salt,

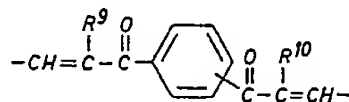
a has the meaning assigned in claim 31,

R^6 represents a valency bond or a hydrogen atom,

Y represents a chain of carbon atoms containing in that chain a grouping of formula



or



R^7 and R^8 are each individually a hydrogen atom, an alkyl group, or an aryl group, or R^7 and R^8 conjointly denote a polymethylene chain of 2 to 4 methylene groups,

R^9 and R^{10} are each a hydrogen atom, an alkyl group, or an aryl group, e and f are each zero, 1, or 2, with the proviso that they are not both zero, and Z is an oxygen or sulphur atom.

33. A method according to claim 18, in which the photopolymerisable component contains at least two groups of the formula



where

R^{11} is an aliphatic or mononuclear aromatic, araliphatic, or heterocyclic group, having ethylenic unsaturation or aromaticity in conjugation with the indicated double bond and R has the meaning assigned in claim 20.

34. A method according to claim 33, in which R^{11} contains up to 12 carbon atoms.

35. A method according to claim 33, in which R^{11} denotes a phenyl, 2-furyl, 2- or 3-pyridyl, or styryl group.

36. A method according to claim 33, in which R^{11} denotes a prop-2-enyl group.

37. A method according to any of claims 17 and 19 to 21, in which there is employed, as photopolymerisation catalyst for the photopolymerisable component, one which, on irradiation, gives an excited state which leads to the formation of free radicals which then initiate polymerisation of the photopolymerisable component.

38. A method according to any of claims 22, 34, and 36, in which there is employed, as photopolymerisation catalyst for the photopolymerisable component, one which, on irradiation, gives an excited state which leads to the formation of free radicals which then initiate polymerisation of the photopolymerisable component.

39. A method according to claim 37, in which the photopolymerisation catalyst is an organic peroxide or hydroperoxide, an α -halogen substituted acetophenone, benzoin or an alkyl ether thereof, a benzophenone, a benzil acetal, or a mixture of a phenothiazine dye or a quinoxaline with an electron donor.

40. A method according to claim 38, in which the photopolymerisation catalyst is an organic peroxide or hydroperoxide, an α -halogen substituted acetophenone, benzoin, or an alkyl ether thereof, a benzophenone, a benzil acetal, or a mixture of a phenothiazine dye or a quinoxaline with an electron donor.

41. A method according to claim 37 or 38, in which the photopolymerisation catalyst is

- an O - alkoxycarbonyl derivative of an oxime of benzil or 1 - phenylpropane - 1,2 - dione.
42. A method according to any of claims 18 and 23 to 33; and 35, in which there is employed, as photopolymerisation catalyst for the photopolymerisable component, on which, on irradiation, gives an excited state which in turn transfers its energy to a monomer molecule giving rise to an excited molecule which then crosslinks with another monomer molecule.
43. A method according to claim 42, in which the photopolymerisation catalyst is 5 - nitroacenaphthene, 4 - nitroaniline, 2,4,7 - trinitro - 9 - fluorenone, 3 - methyl - 1,3 - diaza - 1,9 - benzanthrone, or a bis(dialkyl-amino)benzophenone.
44. A method according to claim 1, substantially as described herein.
45. A method according to claim 1, substantially as described in Example 1 or 2.
46. A method according to claim 1, substantially as described in any of Examples 3, to 5.
47. Prepregs made by a method as claimed in any of claims 1 to 21, 23 to 33, 35, 37, 39, 42, 43, and 45.
48. Prepregs made by a method as claimed in any of claims 22, 34, 36, 38, 40, 41, 44, and 46.
49. A method of making a reinforced composite which comprises heat-curing a prepreg as claimed in claim 47.
50. A method of making a reinforced composite which comprises heat-curing a prepreg as claimed in claim 48.
51. Reinforced composites made by the method of claim 49.
52. Reinforced composites made by the method of claim 50.
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